PATENT SPECIFICATION

NO DRAWINGS

Inventors: GEORGE CHARLESWORTH HAMPSON and FRANCIS ROBERT MAXWELL McDONNELL

864,798

Date of filing Complete Specification: March 19, 1959.

Application Date: March 20, 1958. *No. 8946/58.*

(Patent of Addition to No. 836,988 dated July 26, 1956.)

Complete Specification Published: April 6, 1961.

Index at acceptance:—Classes **15(2)**, A1(A1B5:A3:C1A:D); **and 91**, D2(E:F:G:L:N:P:Q:V), S2(E:F:G:L:N:P:Q:V).

International Classification:—**D06l. C11d.**

COMPLETE SPECIFICATION

Bleaching Processes and Compositions

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to bleaching compositions suitable for removing stains from textile materials and to processes in which they are used.

British Patent Specification No. 836,988 relates to bleaching processes in which there are used aqueous hydrogen peroxide and certain organic esters of carboxylic acids, and also to bleaching compositions containing inorganic persalts and these esters. By means of such processes, bleaching can be carried out under the normal conditions of operation of washing machines, using temperatures of, for example 50°—60°C. The hydrogen peroxide (which when the compositions are used is liberated by the persalt in aqueous solution) reacts with the ester to give a bleaching agent more vigorous than hydrogen peroxide and so promotes low-temperature bleaching.

The esters concerned in Specification No. 836,988 are those which give a titre of at least 1.5 ml. 0.1 N sodium thiosulphate in a test which is described in that specification. Whether any particular ester is one which possesses the properties required depends at least in part upon the precise electronic properties of its molecule, but it has not been found possible to define the esters which are suitable solely in terms of chemical structure. Variation of substituents in the molecule may affect profoundly the behaviour of the ester in the bleaching process. For example, while phenyl benzoate and benzoyl salicylic acid are suitable for use in the bleaching process, phenyl *o*-toluate and phenyl salicylate are not. The sodium thiosulphate titre test, which is described in this specification immediately before the Examples, provides a very simple and convenient method for determining whether a particular ester is suitable. The four specific esters mentioned above have titres in this test of 4.4, 2.0, 0.25, and 0 ml. respectively, thus illustrating the simplicity and effectiveness of the distinction which the test provides. Where a "reactive ester" is subsequently referred to in this specification, there is meant an ester which meets the requirements of the test, namely a titre of at least 1:5 ml. 0.1 N sodium thiosulphate. Accordingly, a "reactive organic ester of an aliphatic carboxylic acid" is an organic ester of an aliphatic carboxylic acid which meets this test. Reactive esters having a titre of more than 3 ml. and as much as 5 ml. or 6 ml. are especially suitable for use in bleaching compositions based on ester and persalt.

The bleaching compositions used in the process described above are conveniently powder mixtures of ester and persalt with or without other materials and which can be added to water immediately before use. For such mixtures the ester itself needs to be one which is solid, that is to say, has a melting point sufficiently above ordinary temperatures to remain solid under normal conditions of storage. The ester and persalt mixed in powder form with other materials are in many instances sufficiently stable towards one another for the solid composition to retain its bleaching properties during storage until it is required for use.

It has however been found that powder compositions containing certain solid esters show a pronounced tendency to decompose during storage. The esters concerned are reactive esters of aliphatic carboxylic acids, which would apart from this serious disad-

vantage be particularly satisfactory for use in the bleaching compositions. The present invention enables this disadvantage to be mitigated or eliminated, for it has now been discovered that the tendency of the ester and persalt to decompose during storage in the presence of one another can be markedly reduced by using the ester in granular form.

The compositions of the invention accordingly are free-flowing solid bleaching compositions which comprise an inorganic persalt and a solid reactive organic ester of an aliphatic carboxylic acid as particles separate from the persalt, the size of the ester particles being such that at least 70% of the ester is retained on a 60 mesh British Standard sieve.

Preferably the ester is one derived from an aliphatic carboxylic acid having not more than 10 and with advantage less than 8 carbon atoms. Normally the acid radical of the ester will be that of a monobasic acid. Esters of acetic acid are particularly susceptible to the decomposition mentioned above, and as it is economically desirable that the acid radical in the ester shall be acetate, the invention is of particular value in relation to them. Examples of other acid radicals which can be present in the esters are propionate, butyrate, caproate and caprylate. Preferably the ester is an acylated phenol. Especially valuable esters are those obtained by the acylation of the phenolic groups in phenol sulphonates, for instance sodium and potassium *p*-acetoxybenzene sulphonate. These esters have a particularly high titre in the test referred to above, and strong bleaching properties at relatively low temperatures are shown by compositions containing them and persalts. The corresponding butyrate, caproate and caprylate can be used instead of the acetoxy compound, and an example of another type of esters which can be used is *p*-acetoxybenzoic acid.

The particle size of the ester is to be such that at least 70% of the ester is retained on a 60 mesh British Standard sieve (a sieve having square apertures of side 251 microns). It is generally convenient to use esters with a particle size such that at least 70% of ester is retained on a 44 mesh British Standard sieve (apertures of side 353 microns), and preferably not so large that less than 70% will pass a 10 mesh sieve (apertures of side 1676 microns). Preferably at least 85% of the ester is of the minimum or maximum particle size concerned, and indeed it is best that particles of smaller size than the lower limit concerned and of larger size than 10 mesh should be substantially completely excluded. The ester used is preferably soluble, that is, one which has a solubility in water at pH 10 of more than 0.1%, especially 1%, or indeed more than 5%, so that dispersions of particles is rapid. In practice, where a relatively water-insoluble ester is used, it should be in a form such that the particles readily break down and disperse when the bleaching composition is used.

The ester can consist of amorphous particles which have been precipitated from solution, for instance during the formation of the ester, of crystals which have been obtained by crystallisation of the ester where this is practicable, or of particles which have been formed by the agglomeration of the powdered ester, for instance as described in one of the Examples below. The desired range of particle sizes can be obtained by using appropriate sieves on a material having a wide distribution of particle sizes. Preferably when the particles are formed by agglomeration a dispersing agent is incorporated in order to assist dispersion when the bleaching compositions containing the ester is added to water for use. A water-soluble binding agent for instance gelatin or starch, can be incorporated in the particles. One method of agglomerating powdered ester is to stir the ester with a small amount of water (or other suitable solvent), pass it through a sieve of appropriate size while it is still in damp condition, and finally dry the granules thus obtained.

The inorganic persalts are salts which give rise to hydrogen peroxide when dissolved in water, and suitable compounds are alkali metal perborates, percarbonates, perpyrophosphates and persilicates. Such salts are believed to contain hydrogen peroxide of crystallisation and may thus not be regarded as true persalts.

Preferably the bleaching compositions of the invention contain a proportion of from $\frac{1}{4}$ to 4, and preferably $\frac{1}{2}$ to $1\frac{1}{2}$, molecules of reactive ester to each atom of available oxygen in the persalt present. A proportion of ester within the range of from 2 to 15 parts by weight to 1 part by weight of hydrogen peroxide available from the persalt is employed in practice. In addition to ester and persalt, the bleaching compositions can contain other materials which it is desired to have present during the bleaching process, for instance inert salts, alkaline substances or detergents. Preferably the compositions contain a solid alkaline substance in an amount such that compositions otherwise similar but without the ester would give a pH within the range 9 to 11 when dissolved at a suitable concentration for bleaching. Suitable alkaline materials are alkali metal carbonates, phosphates and silicates: the phosphates can be orthophosphates or water-soluble condensed phosphates, for instance tripolyphosphates and pyrophosphates. The bleaching compositions can contain an organic detergent which is either a soap or a soapless detergent, for instance an alkylaryl sulphonate or an alkyl sulphate, in sufficient amount so that when the bleaching composition is used the product washes as well as bleaches. The detergent bleaching composition will in practice also contain conven-

tional detergent adjuncts, for example alkali metal sulphates, alkaline substances such as those mentioned above, sodium carboxymethyl cellulose and fluorescent brightening agents.

The proportion of persalt and ester in a detergent will depend upon the conditions of use, the individual materials involved, and the degree of bleaching and washing required. In general a detergent bleaching composition will contain from 10 to 50% by weight of organic detergent, from 2 to 30% of ester and from 1 to 15% persalt, the remainder of the composition consisting of other materials such as detergent adjuncts. In practice the amount of persalt employed should be such that at least 0.1% of available oxygen by weight of detergent bleaching composition is present.

The processes of the invention are those in which the bleaching composition are used to bleach materials, for instance stained cotton fabrics and other stained or soiled fabrics which can be bleached with persalts. For this purpose they are dispersed in water heated to a suitable temperature, for instance 50°—60° C., at a suitable concentration for the particular application concerned. Under most conditions the amount of bleaching composition required should be such as to give a persalt concentration equivalent to from 0.001 to 0.1% available oxygen by weight of the liquor. The bleach or wash liquor in practice should contain added alkali sufficient to give an initial pH within the range 9 to 11 where insufficient alkaline substance to provide this is present in the solid bleaching composition employed. The most effective bleaching action is of course obtained under conditions of effective agitation such as that provided in a washing machine.

Test

The following test is the one mentioned in this specification in connection with the definition of a "reactive ester" as being an ester which has titre of at least 1.5 ml. 0.1 N sodium thiosulphate.

A test solution is prepared by dissolving the following materials in 1000 ml. distilled water:

Sodium pyrophosphate $Na_4P_2O_7.10H_2O$	2.5 g.
Sodium perborate $NaBO_2.H_2O_2.3H_2O$ (having 10.4% available oxygen)	0.615 g.
Sodium dodecylbenzene sulphonate (the dodecyl group being that derived from tetrapropylene)	0.5 g.

To this solution at 60°C. is added an amount of ester such that for each atom of available oxygen present one molecule of ester is introduced. A water-soluble ester or one which is liquid at 60°C. is added directly to the test solution, but other esters are first dissolved in 10 ml. ethyl alcohol and then added to a test solution prepared using 99/ ml. distilled water.

The mixture obtained by addition of the ester is mechanically stirred by means of a ¾" glass stirrer at 600 revs. per minute and maintained at 60°C. After 5 minutes from the addition a 100 ml. portion of the solution is withdrawn and immediately pipetted on to a mixture of 250 g. cracked ice and 15 ml. glacial acetic acid. Potassium iodide (0.4 g.) is then added and the liberated iodine is immediately titrated with 0.1 N sodium thiosulphate solution with starch as indicator until the first disappearance of the blue colour. The amount of thiosulphate solution used is the titre, and an ester which gives a titre of at least 1.5 ml. is a "reactive ester."

The invention is illustrated by the following Examples:

Example 1

This Example illustrates the preparation of an ester in granular form by sieving, and bleaching compositions obtained by mixing the granular ester with a persalt.

Sodium *p*-acetoxybenzene sulphonate was prepared by the acetylation of dry powdered sodium *p*-hydroxybenzene sulphonate with acetic anhydride with heating under reflux for 5 hours. The product obtained by filtering the cooled reaction mixture and drying the residue was highly water-soluble and gave in the test described above of titre of 6.1. The particle size distribution of the ester was determined by sieving with British Standard sieves (see British Standard Specification 410 of 1943), as follows:

Sieve			Quantity by Weight
Passed		Retained	
Mesh	Aperture (microns)	Mesh	
150	104	—	23%
85	178	150	15%
60	251	85	17%
44	353	60	18%
10	1676	44	27%

Two portions of ester of selected particle size ranges were prepared by sieving the bulk product as follows:

A. Retained on a 60 mesh sieve but passing a 22 mesh sieve.

B. Retained on a 22 mesh sieve, but passing a 10 mesh sieve.

A bleaching composition according to the invention was obtained by mixing 3 parts by weight of portion A or portion B with 2 parts of sodium perborate $NaBO_2.H_2O_2.3H_2O$, of particle size such that 70% was retained on a 60 mesh sieve.

EXAMPLE 2

This illustrates bleaching compositions of the invention which contain organic detergents, and their stability on storage as compared with similar compositions prepared from ester of finer particle sizes.

Detergent bleaching compositions were prepared using a spray-dried detergent powder base containing the following materials in parts by weight.

Sodium dodecylbenzene sulphonate (the dodecyl group was that derived from tetrapropylene)	21.9
Anhydrous alkaline sodium silicate	6.6
Tetrasodium pyrophosphate	13.1
Pentasodium tripolyphosphate	21.9
Anhydrous sodium sulphate	24.4
Water	12.1

To a number of portions consisting of 3.6 g. of this detergent powder base was added 0.32 g. of sodium perborate tetrahydrate (containing 10.5% available oxygen) and 0.48 g. of samples of sodium *p*-acetoxybenzene sulphonate of differing particle size, namely (i) unsieved ester obtained as indicated in Example 1, (ii) ester which had been passed through a 150 mesh B.S. sieve, (iii) ester which was wholly retained on a 150 mesh sieve but passed a 60 mesh sieve, (iv) and (v) the sieved ester portions A and B of Example 1 respectively. The five compositions thus obtained were stored separately in open specimen tubes at 28°C. and 70% relative humidity, and the amount of ester and perborate decomposed in each composition after 1 week (a) and also after 2 weeks (b) was determined. The results are given in the following table.

Sample	Ester particle size	% Decomposition			
		Ester		Perborate	
		(a)	(b)	(a)	(b)
(i)	Unsieved	38	47	8	21
(ii)	Finer than 150 mesh	38	59	25	35
(iii)	60 — 150 mesh	19	48	24	33
(iv)	22 — 60 mesh (A)	2	3	2	3
(v)	Coarser than 22 mesh (B)	8	6	3	6

The marked superiority in stability of the detergent bleaching compositions (iv) and (v), which are bleaching compositions of the invention, is clearly demonstrated.

EXAMPLE 3

The unsieved sodium *p*-acetoxybenzene sulphonate referred to in Example 1 was granulated by the following procedure. A portion of the ester (10 g.) was mixed in a beaker with water (3 g.) by stirring it with a glass rod. The homogeneous damp material obtained was pressed through a 10 mesh sieve and the crumbs produced were dried at 120°C. to give granules. These granules were submitted to sieve analysis, with results as follows:

Sieve			Quantity by Weight
Passed		Retained	
Mesh	Aperture (microns)		
150	104	—	4.1%
85	178	150	9.6%
60	251	85	10.9%
44	353	60	12.5%
22	699	44	33.2%
10	1676	22	29.7%

It will be seen that 75.4% of the granular material had a particle size corresponding to between 10 and 60 mesh.

A sample of granules (0.48 g.) was then mixed with sodium perborate (0.32 g.) and the spray-dried detergent powder of Example 2 (3.6 g.); a further sample of the granules which had been sieved to remove particles passing through a 44 mesh sieve was also mixed with sodium perborate and detergent powder in the same way, and the two compositions thus obtained were tested as described in Example 2, in comparison with a similar sample prepared from unagglomerated unsieved ester. After one week's storage, the sample prepared from unagglomerated unsieved ester showed 65% ester decomposition, while the samples containing unsieved granular ester and sieved granular ester showed 27% and 0% decomposition respectively.

EXAMPLE 4

This Example illustrates the improved stability of a bleaching composition consisting of a mixture of ester and persalt when the ester is in granular form.

A composition of the invention was prepared by mixing 1 part by weight of sodium perborate tetrahydrate, of particle size such that 70% was retained on a 60 mesh sieve with 1.5 parts of sodium *p*-acetoxybenzene sulphonate having a particle size such that all of it passed through a 16 mesh sieve but was held on a 44 mesh sieve. For comparison similar compositions were prepared using the same ester of particle size 85—150 mesh, and also of size passing 150 mesh. Two samples of each

composition were stored in open specimen tubes at 28°C. and 70% relative humidity for 6 weeks. The samples were then analysed to determine the extent of decomposition of the ester and perborate, with the results given in the following table.

Ester particle size	% Decomposition	
Mesh	Ester	Perborate
16 — 44	24, 25	35, 33
85 — 150	49, 51	61
Finer than 150	72, 75	80

EXAMPLE 5

This Example illustrates the criticality of the particle size of the ester in detergent bleaching compositions in order to minimize decomposition on storage.

Samples (20.5 g.) of sodium *p*-acetoxybenzene sulphonate of various particle size ranges were mixed with the detergent powder base of Example 2 (180 g.) and sodium perborate tetrahydrate powder (13.8 g.), and stored in duplicate or triplicate in wax laminated cardboard cartons of a kind used as containers for commercial detergent powders at 28°C. and 70% relative humidity for 6½ weeks, after which the extent of their decomposition was determined. The results were as follows.

Ester particle size	% Decomposition	
Mesh	Ester	Perborate
16 — 44	0, 3	16, 11
44 — 60	3, 5	11, 16
60 — 85	10, 17	20, 19
85 — 150	21, 25, 42	27, 24, 29
Finer than 150	43, 47, 34	37, 38, 39

During the same period samples of a composition similar except that it contained no ester had lost 8, 9, and 10% respectively of their available oxygen. The samples of compositions containing the ester of finer particle size ranges showed a tendency to develop a pink colouration on storage.

EXAMPLE 6

This Example illustrates a bleaching process carried out using a detergent bleaching composition of the invention.

A composition was prepared by mixing 100 parts by weight of the detergent powder base of Example 2 with 8.7 parts of sodium perborate tetrahydrate and 13.0 parts of sodium *p*-acetoxybenzene sulphonate of particle size range between 16 and 44 mesh. A 0.45% by weight solution of the composition (containing 0.37% of the detergent powder base, 0.0032% of available oxygen and 0.048% of the ester) was maintained in a thermostat at 60°C. A heavily tea-stained cotton sheeting test cloth was immersed in the solution for 10 minutes and continuously stirred (the ratio of washing liquid to cloth being 20 parts to 1 by weight), after which it was taken out and rinsed in warm distilled water. The increase in reflectance of the dried and ironed cloth was measured with a Hunter reflectometer, using a blue filter.

A similar test was carried out using a 0.40% solution of a composition which was the same except that it contained no ester. The ester-containing composition gave an increase in reflectance of 18.1%, while the composition from which ester was absent gave an increase of 12.8%.

EXAMPLE 7.

This illustrates the use of sodium percarbonate as persalt in detergent bleaching compositions of the invention.

A composition was prepared by mixing 100 parts by weight of the detergent powder base of Example 2 with 6.65 parts of sodium percarbonate (containing 13% available oxygen) and 13 parts of sodium *p*-acetoxybenzene sulphonate having a particle size range of between

16 and 44 mesh. A second composition was prepared in the same way using ester of particle size range 44 to 60 mesh.

The stability of samples of these compositions on storage in open specimen tubes at 28°C. and 70% relative humidity for 7 days was then compared with that of similar compositions containing ester not in granular form. The results were as follows:

Ester particle size	% Decomposition	
Mesh	Ester	Percarbonate
16 — 44	0, 5.5	12, 12
44 — 60	5.5, 11	17, 17
85 — 150	25, 21	30, 28
Finer than 150	40	44

EXAMPLE 8

This and subsequent Examples illustrate detergent bleaching compositions of the invention containing esters other than sodium *p*-acetoxybenzene sulphonate.

Sodium *p*-butyroxybenzene sulphonate was prepared by refluxing anhydrous sodium *p*-phenol sulphonate with excess *n*-butyric anhydride for several hours, filtering the cooled reaction mixture, washing the residue with acetone and drying the product at 120°C. The butyric ester gave a titre of 6.4 in the test described in this specification.

Detergent bleaching compositions were prepared by mixing 100 parts by weight of the detergent powder base of Example 2 but 8.9 parts of sodium perborate tetrahydrate and 15 parts of the butyric ester of particle size ranges 16 to 44 and 44 to 60 mesh respectively. Further compositions were prepared using butyric ester of finer particle size and samples of all the compositions were stored in open specimen tubes at 28°C. and 70% relative humidity for 2 weeks, after which the extent of their decomposition was determined. The results were as follows.

Ester particle size	% Decomposition	
Mesh	Ester	Perborate
16 — 44	0	7
44 — 60	0	10
60 — 85	12	16
85 — 150	12	22

These results illustrate that a particle size range of below 60 mesh is critical for stability of the ester.

EXAMPLE 9

Compositions similar to those of Example 8 but containing the caproic ester of sodium *p*-hydroxybenzene sulphonate instead of its butyric analogue were prepared and tested for stability in the same way. The caproic ester was prepared by heating anhydrous sodium *p*-phenol sulphonate at 200°C. with excess caproic anhydride for several hours, filtering the cooled reaction mixture, and recrystallising the product from aqueous alcohol. The white powder obtained was granulated by stirring 7 parts by weight with 0.9 parts of water, brushing the product through a 10 mesh sieve and drying the resulting particles at 105°—110°C. The required particle size ranges were then sieved out.

The bleaching compositions contained 100 parts of detergent powder base, 8.9 parts of sodium perborate, and 16.4 parts of caproic ester. The results of the stability tests on storage at 28°C. and 70% relative humidity for 4 weeks were as follows.

Ester particle size	% Decomposition	
Mesh	Ester	Perborate
16 — 44	0	13
44 — 60	36	38
60 — 85	40	51
85 — 120	58	48
Finer than 150	68	40

EXAMPLE 10.

Instead of the caproic ester, the corresponding caprylic ester prepared by an analogous method was granulated in the same way, compositions prepared containing 17.8 parts of it to 100 parts of detergent powder base and 8.9 parts of sodium perborate, and the compositions tested as in Example 9, with the following results.

Ester particle size	% Decomposition	
Mesh	Ester	Perborate
16 — 44	0	17
44 — 60	8	28
60 — 85	13	43
85 — 150	26	41
Finer than 150	72	40

EXAMPLE 11

This Example illustrates the use of *p*-acetoxybenzoic acid as ester and the employment of gelatin and starch as binding agents for the granular ester.

p-Acetoxybenzoic acid was obtained from the acetylation of *p*-hydroxybenzoic acid as a powder whose particle size was analysed by sieving as follows.

Particle size range	Quantity
Mesh	%
Finer than 150	10.7
85 — 150	20.6
60 — 85	14.6
44 — 60	20.8
22 — 44	33.3

The unsieved ester was granulated by two methods. In method A, 10 parts by weight of the ester was mixed with 4.8 parts of water, the mixture brushed through a 22 mesh sieve and dried at 105°—110°C. From the product a portion of 16 to 44 mesh particle size range was sieved out. In method B, 10 parts by weight of the ester was mixed with 5.8 parts of an aqueous solution containing 4.5% of gelatin and 4.5% of maize starch; the mixture was brushed through a 20 mesh sieve, dried at 105°—110°C. and the product sieved as before.

Bleaching compositions of the invention

were prepared by mixing 100 parts by weight of the detergent powder base of Example 2 with 8.65 parts of sodium perborate and 9.7 parts of the granular ester obtained by the two methods. The stability of the two compositions was compared with that of a similar composition prepared from the unsieved ungranulated ester, by storing samples of the compositions at 28°C. and 70% relative humidity for 13 days and then analysing them. The following results were obtained.

Ester form	% Decomposition	
	Ester	Perborate
16—44 mesh from method A	0, 3	10, 14
16—44 mesh from method B	10, 4.5	10, 10
Ungranulated	53, 49	48, 49

WHAT WE CLAIM IS:—

1. A free-flowing solid bleaching composition comprising an inorganic persalt and a solid reactive organic ester of an aliphatic carboxylic acid (as herein defined) as particles separate from the persalt, the size of the ester particles being such that at least 70% of the ester is retained on a 60 mesh British Standard sieve.

2. A composition according to Claim 1, in which the particle size of the ester is such that at least 70% of it is retained on a 44 mesh British Standard sieve.

3. A composition according to Claim 1 or Claim 2, in which at least 70% of the ester has a particle size such that it passes a 10 mesh British Standard sieve.

4. A composition according to any one of Claims 1 to 3, in which at least 85% of the ester is of the particle size defined.

5. A composition according to any one of Claims 1 to 3, in which substantially all of the ester is of the particle size defined.

6. A composition according to any preceding claim, which also contains a solid alkaline substance.

7. A composition according to any preceding claim, which also contains an organic detergent.

8. A composition according to any preceding claim, in which the ester is one derived from an aliphatic carboxylic acid having not more than 10 carbon atoms.

9. A composition according to any one of Claims 1 to 8, in which the ester is one derived from an aliphatic carboxylic acid having less than 8 carbon atoms.

10. A composition according to any one of Claims 1 to 8, in which the ester is one derived from acetic acid.

11. A composition according to any preceding claim, in which the ester is an acylated phenol.

12. A composition according to any preceding claim, in which the ester has a solubility in water at pH 10 of more than 0.1%.

13. A composition according to any preceding claim, in which the ester is an acylated phenol sulphonate.

14. A composition according to Claim 13, in which the ester is sodium or potassium *p*-acetoxybenzene sulphonate.

15. A composition according to any preceding claim, in which the persalt is sodium perborate or sodium percarbonate.

16. A composition according to any preceding claim, and containing from ¼ to 4 molecules of ester to each atom of available oxygen in the persalt present.

17. A composition according to any one of Claims 1 to 15, and containing from ½ to 1½ molecules of ester to each atom of available oxygen in the persalt present.

18. A free-flowing solid bleaching composition containing ester having a particle size as defined in Claim 1, substantially as described in any one of Examples 1 to 3.

19. A solid bleaching composition containing ester having a particle size as defined in Claim 1, substantially as described in any one of Examples 4 to 11.

20. A process for bleaching materials, in which a composition according to any preceding claim is dispersed in water and materials are bleached with the liquor obtained.

UNILEVER LIMITED,
R. JONAS,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Bleaching Processes and Compositions

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare this invention to be described in the following statement:—

This invention relates to bleaching composi-

tions suitable for removing stains from textile materials, to processes in which they are used, and also to ingredients suitable for use in the compositions.

British Patent Application 21686/55 and 5571/56 (Serial No. 836,988) relates to bleaching processes in which there are used aqueous hydrogen peroxide and certain organic esters of carboxylic acids, and also to bleaching compositions containing inorganic persalts and these esters. By means of such processes, bleaching can be carried out under the normal conditions of operation of washing machines, using temperatures of, for example, 50°—60° C. The hydrogen peroxide (which when the compositions are used is liberated by the persalt in aqueous solution) reacts with the ester to give a bleaching agent more vigorous than hydrogen peroxide and so promotes low-temperature bleaching.

The esters concerned in Application 21686/55 and 5571/56 (Serial No. 836,988) are those which give a titre of at least 1.5 ml. 0.1 N sodium thiosulphate in a test which is described in that specification. Whether any particular ester is one which possesses the properties required depends at least in part upon the precise electronic properties of its molecule, but it has not been found possible to define the esters which are suitably solely in terms of chemical structure. Variation of substituents in the molecule may affect profoundly the behaviour of the ester in the bleaching process. For example, while phenyl benzoate and benzoyl salicyclic acid are suitable for use in the bleaching process, phenyl *o*-toluate and phenyl salicylate are not. The sodium thiosulphate titre test, which is described in this specification immediately before the Examples, provides a very simple and convenient method for determining whether a particular ester is suitable. The four specific esters mentioned above have titres in this test of 4.4, 2.0, 0.25 and 0 ml. respectively, thus illustrating the simplicity and effectiveness of the distinction which the test provides. Where a "reactive ester" is subsequently referred to in this specification, there is meant an ester which meets the requirements of the test, namely a titre of at least 1.5 ml. 0.1 N sodium thiosulphate. Reactive esters having a titre of more than 3 ml. and as much as 5 ml. or 6 ml. are especially suitable for use in bleaching compositions based on ester and persalt.

The bleaching compositions used in the process described above are conveniently powder mixtures of ester and persalt with or without other materials and which can be added to water immediately before use. For such mixtures the ester itself needs to be one which is solid, that is to say, has a melting point sufficiently above ordinary temperatures to remain solid under normal conditions of storage. The ester and persalt mixed in powder form with other materials are in many instances sufficiently stable towards one another for the solid composition to retain its bleaching properties during storage until it is required for use.

It has however been found that powder compositions containing certain solid esters show a pronounced tendency to decompose during storage. The esters concerned are reactive esters of aliphatic carboxylic acids, which would apart from this serious disadvantage be particularly satisfactory for use in the bleaching compositions. The present invention enables this disadvantage to be mitigated or eliminated, for it has now been discovered that the tendency of the ester and persalt to decompose during storage in the presence of one another can be markedly reduced by using the ester in granular form.

The solid bleaching compositions of the invention accordingly comprise an inorganic persalt and a solid reactive organic ester of an aliphatic carboxylic acid, the ester being in granular form.

Preferably the ester is one derived from an aliphatic carboxylic acid having not more than 10 and with advantage less than 8 carbon atoms. Normally the acid radical of the ester will be that of a monobasic acid. Esters of acetic acid are particularly susceptible to the decomposition mentioned above, and as it is economically desirable that the acid radical in the ester shall be acetate, the invention is of particular value in relation to them. Examples of other acid radicals which can be present in the esters are propionate and butyrate; the esters of higher fatty acids are in general less unstable in the bleaching compositions than the corresponding acetates, but nevertheless the invention is of advantage in respect of them also. Preferably the ester is an acylated phenol. Especially valuable esters are those obtained by the acylation of the phenolic groups in phenol sulphonates, for instance sodium and potassium *p*-acetoxybenzene sulphonate. These esters have a particularly high titre in the test referred to above, and strong bleaching properties at relatively low temperatures are shown by compositions containing them and persalts. The corresponding caproate and caprylate can be used instead of the acetoxy compound, and an example of another type of ester which can be used is *p*-acetoxybenzoic acid.

The reactive ester is to be in granular form, by which it is meant that the ester is to have an average particle size substantially larger than that of a normal powder. In practice the particle size should be such that at least 70% of the ester is retained on a 60 mesh British Standard sieve (a sieve having square apertures or side 251 microns). It is generally convenient to use esters with a particle size such that at least 70% of ester is retained on a 44 mesh British Standard sieve (apertures of side 353 microns), and preferably not so large

that less than 70% will pass a 10 mesh sieve (apertures of side 1676 microns). Preferably at least 85% of the ester is of the minimum or maximum particle size concerned, and indeed it is best that particles of smaller size than the lower limit concerned and of larger size than 10 mesh should be substantially completely excluded. The most suitable particle size for any particular ester is the coarsest which it is mechanically satisfactory to employ bearing in mind the quantity of bleaching composition to be used at any one time, the need for the relative proportion of ester and persalt to be maintained constant within reasonable limits in successive portions taken from a bulk supply, and also the ease with which the particles of ester are dispersible in the aqueous solution used for bleaching. The ester used is indeed preferably soluble, that is one which has a solubility in water at pH 10 of more than 0.1%, especially 1%, or indeed more than 5%, so that dispersion of large particles causes no problem. In practice, where a relatively water-insoluble ester is used, it should be in the form such that the particles readily break down and disperse when the bleaching composition is used. The minimum particle size which the ester is to have in order to reduce the danger of decomposition substantially will vary according to the nature of the ester, but in general the limits of particle size indicated above provide some advantage as compared with finely powdered ester irrespective of the particular ester employed.

The granular ester can consist of amorphous particles which have been precipitated from solution, for instance during the formation of the ester, of crystals which have been obtained by crystallisation of the ester where this is practicable, or of particles which have been formed by the agglomeration of the powdered ester, for instance as described in one of the Examples below. The desired range of particle sizes can be obtained by using appropriate sieves on a material having a wide distribution of particle sizes. Preferably when the particles are formed by agglomeration a dispersing agent is incorporated in order to assist dispersion when the bleaching composition containing the ester is added to water for use. A water-soluble binding agent can be incorporated in the particles. One method of agglomerating powdered ester is to stir the ester with a small amount of water (or other suitable solvent), pass it through a sieve of appropriate size while it is still in damp condition, and finally dry the granules thus obtained.

The granular esters used in the bleaching compositions of the invention have a deliberately selected range of particle sizes and in that form are themselves new materials useful for the special purpose of making the bleaching compositions of the invention. Accordingly the granular esters as defined above are themselves within the scope of the invention.

The inorganic persalts are salts which give rise to hydrogen peroxide when dissolved in water, and suitable compounds are alkali metal perborates, percarbonates, perpyrophosphates and persilicates. Such salts are believed to contain hydrogen peroxide of crystallisation and may thus not be regarded as true persalts.

Preferably the bleaching compositions of the invention contain a proportion of from ¼ to 4, and preferably ½ to 1½, molecules of reactive ester to each atom of available oxygen in the persalt present. A proportion of ester within the range of from 2 to 15 parts to 1 part of hydrogen peroxide available from the persalt is employed in practice. In addition to ester and persalt, the bleaching compositions can contain other materials which it is desired to have present during the bleaching process, for instance inert salts, alkaline substances or detergents. Preferably the compositions contain a solid alkaline substance in an amount such that compositions otherwise similar but without the ester would give a pH within the range 9 to 11 when dissolved at a suitable concentration for bleaching. Suitable alkaline materials are alkali metal carbonates, phosphates and silicates; the phosphates can be orthophosphates or water-soluble condensed phosphates, for instance tripolyphosphates and pyrophosphates. The bleaching compositions can contain an organic detergent which is either a soap or a soapless detergent, for instance an alkylaryl sulphonate or an alkyl sulphate in sufficient amount so that when the bleaching composition is used the product washes as well as bleaches. The detergent bleaching composition will in practice also contain conventional detergent adjuncts, for example alkali metal sulphates, alkaline substances such as those mentioned above, sodium carboxymethyl cellulose and fluorescent brightening agents.

The proportion of persalt and ester in a detergent will depend upon the conditions of use, the individual materials involved, and the degree of bleaching and washing required. In general a detergent bleaching composition will contain from 10 to 50% by weight of organic detergent, from 2 to 30% of ester and from 1 to 15% of persalt, the remainder of the composition consisting of other materials such as detergent adjuncts. In practice the amount of persalt employed should be such that at least 0.1% of available oxygen by weight of detergent bleaching composition is present.

The processes of the invention are those in which the bleaching compositions are used. For this purpose they are dispersed in water heated to a suitable temperature, for instance 50°—60°C., at a suitable concentration for the particular application concerned. Under most conditions the amount of bleaching composition required should be such as to give a persalt concentration equivalent to from 0.001 to 0.1% available oxygen by weight of the liquor. The bleach or wash liquor in practice should

contain added alkali sufficient to give an initial pH within the range 9 to 11 where insufficient alkaline substance to provide this is present in the solid bleaching composition employed. The most effective bleaching action is of course obtained under conditions of effective agitation such as that provided in a washing machine.

TEST

The following test is the one mentioned in this specification in connection with the definition of a " reactive ester " as being an ester which has titre of at least 1.5 ml. 0.1 N sodium thiosulphate.

A test solution is prepared by dissolving the following materials in 1000 ml. distilled water:

Sodium pyrophosphate $Na_4P_2O_7.10H_2O$	2.5 g.
Sodium perborate $NaBO_2.H_2O_2.3H_2O$ (having 10.4% available oxygen)	0.615 g.
Sodium dodecylbenzene sulphonate (the dodecyl group being that derived from tetrapropylene)	0.5 g.

To this solution at 60°C. is added an amount of ester such that for each atom of available oxygen present one molecule of ester is introduced. A water-soluble ester or one which is liquid at 60°C. is added directly to the test solution, but other esters are first dissolved in 10 ml. ethyl alcohol and then added to a test solution prepared using 990 ml. distilled water.

The mixture obtained by addition of the ester is vigorously stirred and maintained at 60°C. After 5 minutes from the addition a 100 ml. portion of the solution is withdrawn and immediately pipetted on to a mixture of 250 g. cracked ice and 15 ml. glacial acetic acid. Potassium iodide (0.4 g.) is then added and the liberated iodine is immediately titrated with 0.1 N sodium thiosulphate solution with starch as indicator until the first disappearance of the blue colour. The amount of thiosulphate solution used is the titre, and an ester which gives a titre of at least 1.5 ml. is a " reactive ester."

The invention is illustrated by the following Examples.

EXAMPLE 1

This Example illustrates the preparation of an ester in granular form by sieving, and bleaching compositions obtained by mixing the granular ester with a persalt.

Sodium *p*-acetoxybenzene sulphonate was prepared by the acetylation of dry powdered sodium *p*-hydroxybenzene sulphonate with acetic anhydride with heating under reflux for 5 hours. The product obtained by filtering the cooled reaction mixture and drying the residue was highly water-soluble and gave in the test described above a titre of 6.1. The particle size distribution of the ester was determined by sieving with British Standard sieves (see British Standard Specification 410 of 1943), as follows.

Sieve			Quantity by weight
Passed		Retained	
Mesh	Aperture (microns)	Mesh	
150	104	—	23%
85	178	150	15%
60	251	85	17%
44	353	60	18%
10	1676	44	27%

Two portions of ester of selected particle size ranges were prepared by sieving the bulk product as follows:

A.	Retained on a 60 mesh sieve but passing a 22 mesh sieve.
B.	Retained on a 22 mesh sieve, but passing a 10 mesh sieve.

A bleaching composition according to the invention was obtained by mixing 3 parts by weight of portion A or portion B with 2 parts of sodium perborate $NaBO_2.H_2O_2.3H_2O$ in finely powdered form.

EXAMPLE 2

This illustrates bleaching compositions of the invention which contain organic detergents, and their stability on storage as compared with similar compositions prepared from finely powdered ester.

Detergent bleaching compositions were prepared using a spray-dried detergent powder base containing the following materials in parts by weight.

Sodium dodecylbenzene sulphonate (the dodecyl group was that derived from tetrapropylene)	21.9
Anhydrous alkaline sodium silicate	6.6
Tetrasodium pyrophosphate	13.1
Pentasodium tripolyphosphate	21.9
Anhydrous sodium sulphate	24.4
Water	12.1

To a number of portions consisting of 3.6 g. of this detergent powder base was added 0.32 g. of sodium perborate tetrahydrate (containing 10.5% available oxygen) and 0.48 g. of samples of sodium *p*-acetoxybenzene sulphonate of differing particle size, namely (i) unsieved ester obtained as indicated in example 1, (ii) ester which had been passed through a 150 mesh B.S. sieve, (iii) ester which was wholly retained on a 150 mesh sieve but passed a 60 mesh sieve, (iv) and (v) the sieved ester portions A and B of Example 1 respectively. The five compositions thus obtained were stored separately in open specimen tubes at 28°C. and 70% relative humidity, and the amount of ester and perborate decomposed in each composition after 1 week (a) and also after 2 weeks (b) was determined. The results are given in the following table.

		% Decomposition			
		Ester		Perborate	
Sample	Ester particle size	(a)	(b)	(a)	(b)
(i)	Unsieved	38	47	8	21
(ii)	<150 mesh	38	59	25	35
(iii)	60—150 mesh	19	48	24	33
(iv)	22—60 mesh (A)	2	3	2	3
(v)	>22 mesh (B)	8	6	3	6

The marked superiority in stability of the detergent bleaching compositions (iv) and (v), which are bleaching compositions of the invention, is clearly demonstrated.

EXAMPLE 3

The unsieved sodium *p*-acetoxybenzene sulphonate referred to in Example 1 was granulated by the following procedure. A portion of the ester (10 g.) was mixed in a beaker with water (3 g.) by stirring it with a glass rod. The homogeneous damp material obtained was pressed through a 10 mesh sieve and the crumbs produced were dried at 120°C. to give granules. These granules were submitted to sieve analysis, with results as follows:

Sieve			Quantity by weight
Passed		Retained	
Mesh	Aperture (microns)		
150	104	—	4.1%
85	178	150	9.6%
60	251	85	10.9%
44	353	60	12.5%
22	699	44	33.2%
10	1676	22	29.7%

It will be seen that 86.3% of the granular material had a particle size corresponding to between 10 and 60 mesh.

A sample of the granules (0.48 g.) was then mixed with sodium perborate (0.32 g.) and the spray-dried detergent powder of Example 2 (3.6 g.); a further sample of the granules which had been sieved to remove particles passing through a 44 mesh sieve was also mixed with sodium perborate and detergent powder in the same way, and the two compositions thus obtained were tested as described in Example 2, in comparison with a similar sample prepared from unagglomerated unsieved ester. After one week's storage, the sample prepared from unagglomerated unsieved ester showed 65% ester decomposition, while the samples containing unsieved granular ester and sieved granular ester showed 27% and 0% decomposition respectively.

UNILEVER LIMITED,
R. JONAS,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.